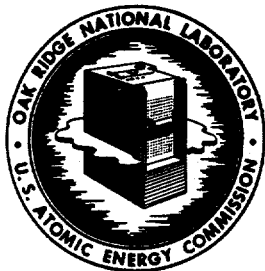


1786

426 (Revised 1-52)

~~SECRET COVER SHEET~~
~~SECURITY INFORMATION~~OAK RIDGE NATIONAL LABORATORY
Operated By
CARBIDE AND CARBON CHEMICALS COMPANY

UCC

POST OFFICE BOX P
OAK RIDGE, TENNESSEE**ORNL**
CENTRAL FILES NUMBER
58.7. 188

DATE: July 28, 1953

COPY NO.

SUBJECT: Chemical Development Status Report
for Week Ending July 17, 1953"This document consists of 6 pages
No. 17 of 24 copies, Series A

TO: F. L. Culler

FROM: F. R. Bruce

DISTRIBUTION:

1. F. L. Culler
2. R. E. Blanco
- 3-4. F. R. Bruce
5. O. C. Dean
6. W. K. Eister
7. D. E. Ferguson
8. J. R. Flanary
9. H. E. Goeller
10. A. T. Gresky
11. I. R. Higgins
12. H. K. Jackson
13. W. B. Lanham
14. R. E. Leuze
15. J. A. McLaren
16. D. C. Overholt
17. C. E. Winters
- 18-19. Laboratory Records Department
20. Laboratory Records Department (ORNL-RC)
- 21-22. Central Research Library
- 23-24. Central Files - Y-12

INV.
52

CLASSIFICATION CANCELLED

DATE 8-22-62*Edgar J. Murphy*CO-ORDINATING ORGANIZATION DIRECTOR
OAK RIDGE NATIONAL LABORATORY
AUTHORITY DELEGATED BY AEC 9-10-57*J.M.*This document has been approved for release
to the public by:*David R. Hamlin* 5/19/95
Technical Information Officer Date
ORNL Site~~RESTRICTED DATA~~This document contains Restricted Data
as defined in the Atomic Energy Act of
1946. Its transmittal or the disclosure
of its contents in any manner to
an unauthorized person is prohibited.~~SECRET COVER SHEET~~
~~SECURITY INFORMATION~~

ChemRisk Document No. 1786

SUMMARY

Purex

A study of the stability of the Purex 1A extraction operation at elevated temperature has been undertaken upon request by duPont. The results of closely controlled batch-countercurrent operation at 35°C, the maximum expected in the SR 1A contactor, show no tendency toward incomplete uranium extraction. Further investigation is planned to determine the combined effect of heating plus the maximum deviations of concentrations and flowrates expected in plant operation upon stability.

Thorium Blanket Studies

A new type abrasion tester using a jet of slurry impinging on a thin foil has been constructed and is now being successfully used. While thorium oxide prepared by calcination of thorium oxalate is abrasive to stainless steel, thorium oxide prepared by hydrolysis in water at 250°C of the hydroxide or carbonate are apparently non-abrasive. The addition of fluoride to thorium oxide slurry has two interesting results at 250°C, the settled volume of the slurry increases and the fluoride leaches uranium from mixed uranium-thorium oxide.

Thorex

The following materials have been found to limit the adsorption of Pa by silica gel: Nb, Fe⁺³, Cr⁺³, Mg⁺², Ca⁺², H₂O₂, HIO₄ and H₂C₂O₄ - PO₄⁻³, SO₄⁻² and CrO₄⁻² assist the adsorption. Oxidation numbers appear to be a reasonable criterion for determining relative stability of organic diluents for TBP.

RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmission or the disclosure of its contents in any manner to an unauthorized person is prohibited.

RESTRICTED DATA

HRE Fuel Recovery

A total of 612 grams of uranium have now been successfully processed in the Cell 4 equipment. In the first hot run 475 grams of uranium were processed from the HRE fuel solution. The uranium loss for this run was less than 0.01% and no detectable fission product activity is on the resin column with the uranium product.

1.0 PUREX

Upon request by duPont, the Purex group has started investigation of the effect of thermal heating on the stability of the ORNL-846 1A flowsheet. Batch equilibrium data previously collected and reported in ORNL-1481 showed that, with a temperature increase from 25 to 50°C, the uranium extraction coefficient is reduced about two-fold whereas Pu(IV), fission products, and HNO_3 extraction increase slightly. With warming of active feed by steam jetting and subsequent mixing with cool streams (solvent and scrub), the ambient temperature of the solution mixture in the 1A contactor at Savannah River is estimated at 35°C. Therefore, the current study of 1A flowsheet stability, product recoveries and decontamination is being conducted at that temperature.

To study the temperature effect with both active and non-active feeds, the vacuum-transfer batch-countercurrent battery at Bldg. 3550 has been enclosed in a hood, heated and thermostated for operation at $35 \pm 1^\circ\text{C}$. The "Lucite" front panel is equipped with glove ports so that manual operation is performed at constant temperature; solutions are metered by burettes with $\pm 0.5\%$ accuracy. Standardized stock solutions of non-active feed (natural uranium and HNO_3), scrub and solvent were prepared for the first series of runs.

The results of three successive runs at 35°C, simulating the ORNL-846 1A operation with closely regulated conditions, showed no tendency toward incomplete extraction of uranium. Approach to steady-state was normal; uranium loss through five extraction stages averaged $5 \times 10^{-5}\%$. Periodic uranium analyses of the

aqueous layer at the third extraction stage (usually sensitive to any shift in uranium extraction at the feed stage or above) showed that countercurrent extraction proceeded smoothly throughout the run. Uranium material balance calculated from potentiometric analyses and stream volumes averaged 97%.

These results demonstrate that complete uranium recovery is attained at 35°C with the ORNL-846 flowsheet if precise control of the flowsheet variables (concentration and flowrate) is maintained. Such control cannot be maintained in plant operation, however, and the combined effect of heating plus the maximum expected flowsheet variations remains to be determined.

2.0 THORIUM BLANKET STUDIES

The purpose of the slurry development program is to produce a non-erosive, non-corrosive, easily dispersed aqueous thorium slurry chemically stable at 250°C and at a concentration of 500-1000 g Th/liter. The thorium compound which appears at first glance most likely to fulfill the above criteria is thorium oxide with the exception that the material as ordinarily prepared by the calcination of thorium oxalate has proven to be highly abrasive to stainless steel. Hence, the first phase of this program has been to investigate the various methods of preparing thorium oxide in an effort to produce a non-abrasive material and to develop an accelerated abrasion test in order to evaluate these studies. This part of the program is well in hand in that the general pattern of thorium oxide chemistry at 250°C in water is becoming clear and a new type abrasion tester involving a jet impingement has been constructed and is now in use.

Numerous experiments have been performed which will be discussed in detail in the subsequent quarterly report. Oxides produced by calcination in general are little changed by hydrolyses in water at 250°C and show a low settled volume. (1500-2000 g Th/liter) Experiment on the effect of calcination temperature on the abrasive properties are in progress but it is still too early for a definite answer as to whether a low-burned oxide would be a

suitable slurry material.

Oxide produced by the hydrolysis in water at 250°C of the hydroxide or carbonate are bulky (400-500 g Th/liter) and apparently non-abrasive. One point which will be investigated immediately is the effect of prolonged hydrolysis at 250°C on the abrasiveness of the hydrolyzed hydroxide. It should be noted that if the hydrolysis products of the hydroxide or carbonate are allowed to dry they become crystalline and lose their desirable properties of low bulk density, slurriability and probably non-erosive characteristics.

A study of the effect of adding fluoride to the oxide in the form of ThF_4 , NaF , and LiF in low F to Th ratios and autoclaving them in water at 250°C is underway and appears of interest in the higher settled volumes obtained and the fact that the alkali fluorides are able to leach uranium from uranium-thorium mixed oxides upon hydrolysis at 250°C.

3.0 THOREX

3.1 Pa Adsorption on Silica Gel

Continuing studies of interferences affecting silica gel adsorption of Pa from synthetic AP streams have indicated that magnesium and calcium are limiting. Beryllium, a member of the same family and known to be present in significant concentration in the AF (0.077 M) is also being checked.

Other additives found limiting adsorption were H_2O_2 , H_5IO_6 and oxalic acid. Na_2CrO_4 was rechecked and found to benefit adsorbability.

A summary of materials affecting adsorption follows: Nb , Fe^{+3} , Cr^{+3} , Mg^{+2} , Ca^{+2} , H_2O_2 , HIO_4 and $\text{H}_2\text{C}_2\text{O}_4$ interfere; PO_4^{-3} , SO_4^{-2} and CrO_4^{-2} assist.

3.2 Diluent Stability

Use of oxidation numbers may appear as a reasonable criterion for relating

stability of raw and preconditioned organic diluents for TBP. Plots of oxygen consumption versus contact times with acidic aqueous solutions of KMnO_4 and $\text{Na}_2\text{Cr}_2\text{O}_7$ present slopes thought to be characteristic of highly unstable diluent impurities and/or relative stability of the primary organic fractions of the diluent. These data will be used to supplement other evaluations of five or six diluent materials under study.

F. R. Bruce

F. R. Bruce

FRB/jr